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EFFECTS OF SOME ELECTROLYTES ON KAOLIN AND THE PROBABLE RELATION TO THE SOIL

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EFFECTS OF SOME ELECTROLYTES ON KAOLIN AND THE PROBABLE RELATION TO THE SOIL

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In a previous paper (22) evidence was presented indicating that the formation of hardpan in clay soils was a function of the pH. In soils observed in the vicinity of Philadelphia, the clay particles forming the hardpan are bound either by iron or aluminum, as the oxides or silicates. They present a layer that is practically impermeable to water and are a factor in local plant distribution, because, severed from the connection with the subsoil, they can dry out more thoroughly and thus cause a higher osmotic pressure, and, it was believed, because iron and aluminum were in the soil solution in sufficient quantities to be toxic to some plants. In a recent article Magistad (15) contributed toward the toxicity problem. This paper deals with a preliminary physical chemical consideration of the behavior of kaolin in an effort to explain how hardpans are formed in acid clay soils.

NATURE OF THE HARDPAN

The hardpan in question occurs in silt and clay loams which have become acid. It is found as a red or silvery layer at various distances below the surface, but is most common at depths of 6 to 20 inches. The layer is made up of clay aggregates more or less cemented by the silicates and oxides of aluminum and iron. When dry, the layer is exceedingly hard, and, soaked in water, becomes tough. In both conditions it is impermeable to water so that the surface soil, even a short time after a rain, loses most of its capillary moisture, while the subsoil immediately below the layer generally has a maximum supply.

In the Philadelphia region, where this hardpan occurs, no succulents survive the summer months.

The surface 6 inches of the soil is generally coarsely granular and dry and relatively free of organic matter. When saturated it tends to puddle and is most unsatisfactory to work.

ADAPTABILITY OF KAOLIN FOR EXPERIMENTS

Several methods of fractionating soils were tried but the same type and size of particle was not consistently obtained. Although, in all the soils used,

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when well washed in distilled water, the particles migrated toward the anode in an electric field, yet they migrated at different rates in samples of soil prepared in the same way at different times. Results obtained with one sample could not be compared with observations made on a different batch of what was apparently the same material. As reproducible results are imperative, it is necessary that the material be of a uniform quality. Soil samples proved impractical and as a substitute, the kaolin supplied by Merck and Company was used. It is fairly uniform in texture and chemically is nearly free of everything except HCl.

It is believed that any conclusions that may be drawn when kaolin[1] is used as the medium are applicable to "clays" as a class. According to Washburn (27), one of the most common mineralogical constituents of "clay" is kaolin, which in its purest form is a crystalline mineral having the composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Warington (26) states that "in a typical clay (kaolin) derived from the decomposition of felspar, the whole substance has practically the same chemical composition. . . . ." Merrill (18) says, "orthoclase is one of the commonest and most abundant of the felspars and forms an essential constituent of acid rocks. . . . . As a rock constituent, the potash felspars are of primary importance yielding on their decomposition . . . . the material kaolin. . . . . "

According to Hall (6) and Hilgard (9) orthoclase may be written $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. It decomposes in carbonated water forming kaolinite, $Al_2O_2(OH)_4 \cdot Si_2O_3$, the basis of clay. Swanson (23) gives another formula for kaolinite and graphically writes it differently from other authorites. It has been suggested that kaolin may be a loose Van Bemmelen (24, 25) adsorption compound of aluminum oxide and sand which may behave as a unit although it is not necessarily one.

The structure of kaolin seems doubtful but it is an important constituent of nearly all clay soils.

METHODS

Determinations were made simultaneously on the same sample of kaolin for:

1. Turbidities at intervals up to forty minutes,
2. Final volumes of the sedimented kaolin at various intervals up to two days,
3. Conductivity, always comparing to blanks containing no kaolin,
4. pH,
5. Sign and intensity of the charge on the particles.

The kaolin was put into collodion bags and dialyzed in a stream of running water for eight weeks. The conductance of the supernatant liquid in which the kaolin was kept was only slightly lower than that of distilled water exposed the same length of time although protected from dust. It was believed that the kaolin so prepared was "chemically pure" and that it did not ionize appre-

ciably. Kaolin was later prepared in an electric dialyzer (17), and washed several times by decantation. So prepared, its resistance is practically the same as that of freshly distilled water. A stock was thus easily prepared.

Determined stock solutions of aluminium chloride, calcium chloride, barium chloride, sodium chloride, hydrochloric acid, and sodium hydroxide were made up and the same solutions were used throughout the work. The sodium hydroxide solution was redetermined from time to time. The stock solutions were diluted with distilled water to give the required concentrations. The concentrations of the other solutions used were only approximately accurate.

A large number of 50-cc. graduated cylinders were procured and twenty chosen having the same internal depth, so that the internal friction in any check experiments would be the same through any given time interval. By means of a pipette, 2 gm. of kaolin were put into each of these graduates, and made up to the 50-cc. mark with the proper solution. In all cases two graduates with kaolin and distilled water were prepared as a check. The graduates were then tightly stoppered by inverting slightly oversize, pliable rubber stoppers into the openings. In this way the stoppers made a flat surface entirely across the mouth of the cylinders. This prevented kaolin from sticking to the much greater surface exposed by variously tapering stoppers. It was assumed that the same quantity of kaolin adhered to the stoppers in all cases. An error was introduced, but a constant one well within the limit of accuracy demanded by the experiments.

1. Turbidities as determined in these experiments are entirely comparative. The standard of comparison chosen was distilled water. Six concentrations of three electrolytes were generally prepared simultaneously when strictly comparative data was wanted. The kaolin was thoroughly shaken in the graduates three or four times at intervals before observations were made. Turbidities were compared at 2, 4, 7, 10, 15, 20, 25, 30, and 40 minutes and, when necessary, longer. The graduates were placed in front of a bank of 25-watt lamps. Black paper was placed behind the graduates so that a good contrast could be had under uniform conditions. After some little practice, it was possible to determine by simply observing turbidities, not only the concentration of the solutions but which solutions were in any given cylinder.

2. The volumes occupied by the kaolin in falling were determined at the same intervals as the turbidities and also at 12, 24, and 48 hours. The bulk of the kaolin settled together leaving a more or less dense supernatant liquid.

3. When the liquid was entirely clear, it was pipetted out and put into a tall, narrow beaker having a capacity of about 30 cc. The resistance in ohms of the liquid was recorded. The resistance in ohms of the same concentration of the liquid before determined, treated in the same way but with no addition of kaolin, was obtained. This gave an immediate and exact comparison of the degree of adsorption or non-adsorption of the electrolyte by kaolin.

4. Determinations for pH were made by means of the potentiometer using

a saturated calomel cell. With the unbuffered solutions, results were entirely unreliable and only those results are recorded which are dependable.

5. Migration measurements were made by means of the apparatus recommended by Northrop (21). The cell used had a depth of 0.2 mm. The particles were observable under the low power of the microscope and migrated at a fair rate in an electric field of 110 volts and 0.3 amperes. The field of the scope was graduated and a graduated glass disc was inserted just beneath the eye piece. By means of a stop watch it was then possible to determine the time required for particles to move a given distance. No observations were made on particles within 55μ of the upper and lower surfaces of the cell. Thus starting at a depth of 55μ from the top of the cell, determinations were made at intervals of 10μ at 10 depths. As many determinations of the rate of movement of the particles as possible were made at all the depths mentioned with the same sample. Because of the rapid settling of the particles, very few determinations could be made in some solutions at the upper levels. In such cases samples were made until the speed of at least ten particles could be observed.

The poles were changed at intervals and the rate of migration noted in the opposite direction. The mean rate of all depths of three or more separate experiments are recorded for each concentration used. As the particles are far from spherical and as in some solutions they form aggregates whereas in others they are very much dispersed, no attempt to calculate the intensity of the charge was made. In all cases the rates recorded are relative to the rate of migration of particles in distilled water.

The figures recorded in table 1 are believed dependable for the weaker solution, but are not satisfactorily reproduced at concentrations of 0.1 *M* or more. Particularly is this true in the case of HCl.

RESULTS

The results reported in table 1 are believed typical for kaolin treated as described. The figures for resistance are the mean of many determinations made on at least three separate check experiments. Final volume results are the mean of two or more readings on at least five check experiments. This also applies to the data on turbidity. It was hoped that pH determinations would be sufficiently accurate to indicate the possibility of the selective adsorption of ions by kaolin. As no reasonable checks were obtained, only the pH limits of the solutions of salts are recorded.

1. It was found that the effects of different solutions on the quantity of kaolin suspended were most apparent 15 minutes after the last shaking. As the bulk of the kaolin settled in the graduates there remained suspended sufficient kaolin particles to color the liquid. A liquid such as 0.001 *M* Al cleared immediately after shaking. The "turbidity" of this solution is recorded as *0*. Less clear solutions were arbitrarily assigned a number as they

TABLE 1

MOLAR SALT CONCENTRATION		OHMS − KAOLIN	OHMS + KAOLIN	VOLUME OF SEDIMENT AT 24 HOURS	TURBIDITY AT 15 MINUTES	TURBIDITY AT 30 MINUTES	SPEED PER SECOND	pH
				cc.			μ	
Water		80,000	13,500	7.30	7	2	−14.5	8.4
NaOH	1.0	—	6	5.94	5	1	−12.9	
	0.3	13	14	5.58	6	1	−14.5	
	0.1	41	45	5.67	7	2	−16.7	
	0.03	114	137	6.75	7	3	−20.5	
	0.01	396	491	6.93	14	6	−26.0	
	0.003	1,755	1,720	6.39	28	12	−28.0	
NaCl	1.0	—	12	6.25	10	2	−10.4	8.4
	0.3	25	30	5.72	9	3	−23.3	
	0.1	76	90	6.24	9	3	−24.5	
	0.03	232	274	7.34	8	2	−21.6	
	0.01	—	716	7.44	7	2	−21.6	
	0.003	1,912	1,820	7.45	6	2	−20.2	8.5
HCl	1.0	—	3	5.58	7	1	+16.0	
	0.3	7	6	6.00	6	1	+	
	0.1	22	26	6.84	2	1	−	
	0.03	61	76	7.59	2	1	−	
	0.01	205	355	7.23	3	1	−	
	0.003	600	2,020	6.78	4	1	−11.3	
$CaCl_2$	0.6	—	12	5.86	9	1	+8.9	7.5
	0.1	45	56	6.30	4	1	−5.7	
	0.03	132	166	6.43	3	1	−7.1	
	0.01	—	450	6.68	3	1	−8.6	
	0.003	1,080	1,166	6.68	4	1	−10.2	
	0.001	3,040	2,810	6.76	5	1	−10.3	
	0.0003	8,800	4,880	6.86	6	1	−10.8	8.5
$BaCl_2$	0.6	—	10	5.76	9	2	+3.0?	
	0.1	44	—	6.35	6	1	−4.5	
	0.03	120	130	6.61	4	1	−	
	0.01	376	410	6.61	2	1	−7.7	
	0.003	1,020	1,101	6.53	3	1	−10.8	
	0.001	3,340	3,050	6.53	4	1	−12.9	
	0.0003	7,950	5,970	6.26	6	1	−15.0	
$AlCl_3$	0.6	7	8	6.52	11	4	+6.9	2.07
	0.1	21	26	7.94	8	3	+19.2	
	0.03	62	72	8.86	8	3	+29.5	
	0.01	—	190	8.90	8	3	+29.5	
	0.003	433	515	9.92	7	2	+32.0	
	0.001	1,210	1,400	10.74	0	0	+21.2	
	0.0003	3,040	2,520	8.02	2	1	−12.3	8.00

increased in turbidity. At 15 minutes from shaking, the graduate containing 0.3 *M* NaOH was less turbid than the graduate containing water. The value *6* is assigned for the turbidity of 0.3 *M* NaOH and *7* for kaolin and distilled water. The turbidity value for water is kept constant for the comparison of check experiments.

The turbidity value of kaolin in water after the 30-minute interval is placed at *2*, and perfect clarity of the supernatant liquid at *0*.

It is then clear that in all the solutions recorded in table 1 (except NaOH) the particles of kaolin settle more or less rapidly. It is also evident that different concentrations of the same electrolyte affect turbidities to a marked extent. With HCl, $CaCl_2$, $BaCl_2$, and $AlCl_3$ there is a concentration producing the least turbidity. Any increase or decrease from this concentration results in an increase in turbidity. It is significant to note that the least concentrated solution of NaCl produces the clearest solution, whereas the most concentrated solution of NaOH produces the least turbidity.

Al is the most efficient ion in clearing solutions of kaolin, followed by Ba, Ca, and H in the order given. With turbidities as criteria, the efficiency of the ions in clearing solutions reduced to simplest terms if H-1, Ba-3, Al-100. Ca is less efficient than Ba in this regard.

NaCl and particularly NaOH, greatly increase the turbidities of the solutions. Even traces of NaOH have a marked effect on kaolin, keeping quantities in suspension for two hours or longer.

Sodium sulfate behaves as NaOH, greatly increasing the turbidity of the solutions. Sodium citrate, even in concentrations of 0.001 *M*, causes the greatest increase in turbidity and prevents clearing for 10 days and sometimes longer.

Sucrose and urea have no effect on turbidities in weaker concentrations. The increase in the specific gravity of the more concentrated solutions tends to keep the particles in suspension for a slightly longer time than distilled water. Thus non-electrolytes have no effect on the clarity of the supernatant liquid.

These results are entirely as could be predicted and are used only as checks on the effect of ions of different speed and valency and as criteria of the relative degree of disassociation of the kaolin aggregates.

2. The concentrations of less than 0.03 *M* Na and H have approximately the same aggregate result, that is, little changing of the final volume of the sediment as compared to water. The OH ion decidedly decreases the final volume of the sediment as do the Ca and Ba ions. The SO_4 ion has a marked reducing effect on the final volume of the sediment whereas the tri-valent citrate ion reduces the volume by almost 50 per cent.

Of the ions used, Al alone increases the volume of the sediment to a marked extent.

The more concentrated solutions of all the salts used decrease the final

volume of the sedimented kaolin very considerably either compared to water or to the less concentrated solutions of the same salt.

Sucrose and urea had no affect whatever on the volume of the sediment produced, the values obtained in all concentrations being the same as those obtained with water. Having no tangential value, the curves are not drawn.

From the curves of figure 1, it may be seen that the volume occupied by 2 gm. of kaolin may be only 60 per cent of that volume attained in water, or it may have increased 50 per cent. Microscopic examination shows that such great differences are due to the formation of sizable aggregates in the case of the greatest increase in the final volume of the sediment, and to the complete break-up of the aggregates when the final volume is markedly decreased.

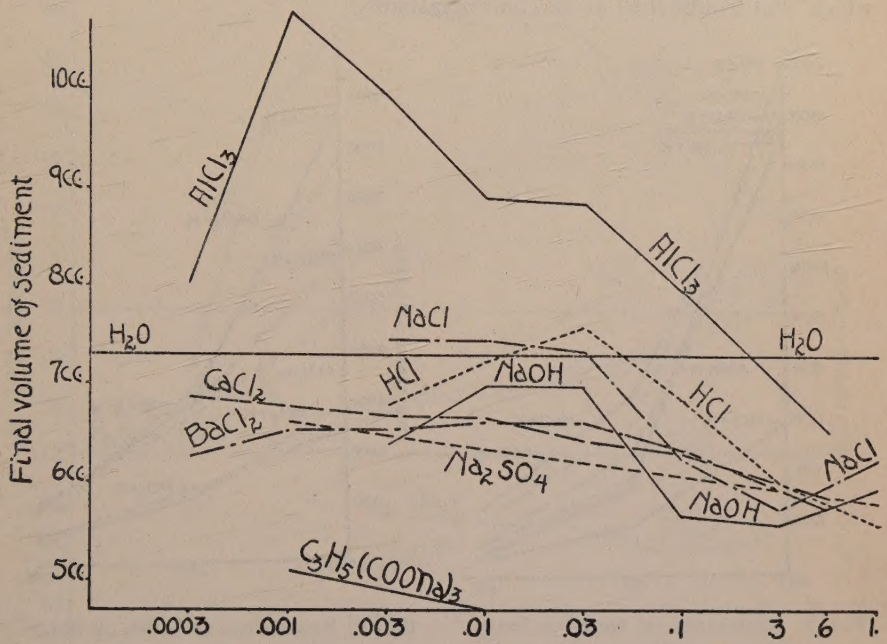

FIG. 1. FINAL VOLUME OF SEDIMENTED KAOLIN IN GRADUATES AT END OF 24 HOURS AFTER SHAKING WITH MOLAR CONCENTRATIONS OF ELECTROLYTES INDICATED

In a general way, it may be said that the more turbid is the supernatant liquid, the less will be the final volume of the sediment.

The experiments on turbidities and sediment volumes furnish a fair check on each other, and are important to this paper only as they indicate that the degree of aggregation of the kaolin particles can be markedly altered, that active anions can break up the aggregates—a tri-valent anion most completely, and a di-valent anion to a greater extent than the OH ion. Of the cations used, Al and Na alone cause the flocculation of the particles.

3. Figures 2 and 3 show that in the weaker solutions of the electrolytes (HCl excepted) no adsorption of the electrolytes occurs. On the contrary,

the solutions apparently become more concentrated in the presence of kaolin. These findings are in accord with those of many investigators working with substances other than kaolin, and again demonstrate that the Freundlich adsorption isotherm does not hold for dilute solutions.

No comparison of adsorption rates of the electrolytes can be made by this method, insofar as adsorption occurs only in the more concentrated solutions where the conduction is too great for accuracy. However, the method furnishes a good comparison of the "negative adsorption" of the salts. This seems to be a false term, for in such solutions something must be adsorbed—if not the solute, then the solvent. However, the following "negative adsorption" sequence may be written: NaCl, NaOH > $BaCl_2$ > $AlCl_3$, > Hcl, in which HCl is adsorbed at all concentrations.

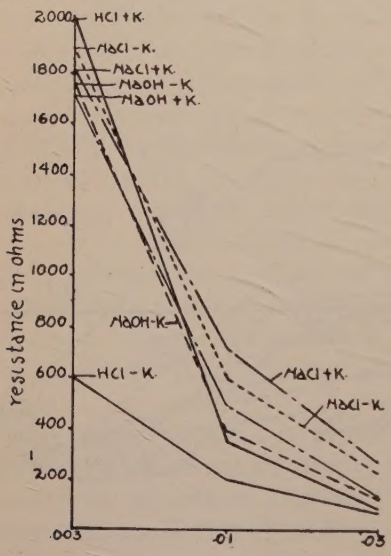

FIG. 2. RESISTANCE IN OHMS OF SOLUTIONS WITH AND WITHOUT KAOLIN AT VARIOUS MOLAR CONCENTRATIONS

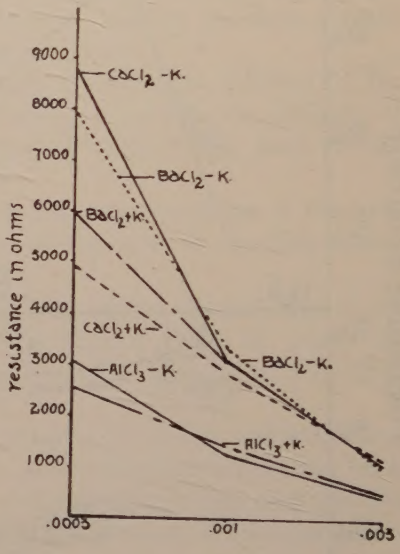

FIG. 3. RESISTANCE IN OHMS OF SOLUTIONS WITH AND WITHOUT KAOLIN AT VARIOUS MOLAR CONCENTRATIONS

It is significant to note that adsorption occurs in weaker solution of Al than of Ba and Ca. A fairly concentrated solution of Na must be present before it is adsorbed by kaolin.

4. The pH of kaolin when dialyzed as described is slightly greater than 8.4. Dilute solutions of the chlorides of Na, Ba, and Ca have little effect on this value. Increased concentrations of $AlCl_3$ rapidly decrease the pH of the kaolin solution but as the curve obtained is very irregular and is believed to be unreliable, it is not recorded. The few pH values reported were checked innumerable times and consistently gave the same figures. They are believed to be reliable, and are accurate within quite narrow limits Ba behaves practically as Ca.

5. Cataphoretic measurements are reported in microns per second. The accuracy of the values given depends entirely on the number of determinations made at the different levels. The greater the number of determinations, the less is the chance of error and the closer is the approach to an absolute comparison. Most of the figures given represent an average of more than 100 observations at 10 levels from three or more separate samples. Comparative results are reproducible within narrow limits, but there is difficulty in obtaining specific values.

A considerable error is obtained in the more concentrated solutions, because

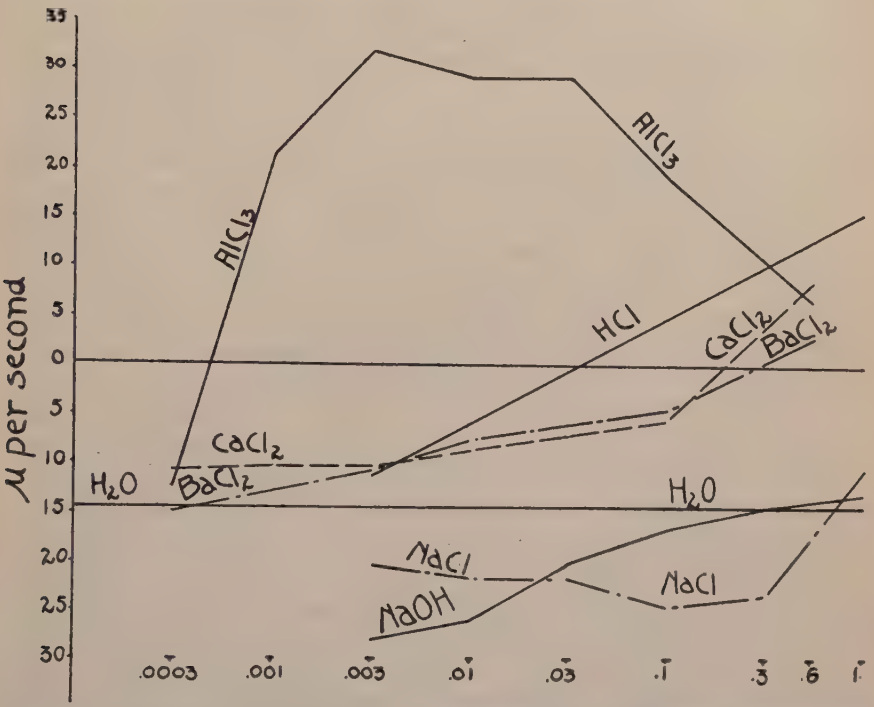

Fig. 4. Rate of Migration of Kaolin Particles in ± μ Per Second When Effected by Molar Concentrations of Electrolytes

of the physical nature of the electrolyte in retarding the particles. The true speed of the particles is believed to be somewhat decreased. Then, too, the size of the particles varies in different solutions and the mass of the particles introduces an error. It was only with the greatest difficulty that any figures at all could be obtained for HCl. This acid appears to neutralize the charge of the particles very completely, causing no motion whatever in most cases, although the particles remain suspended. It was clearly seen that in the same solutions at any given level, particles migrated to both the anode and cathode. Indeed the same particle could change the sign of its charge several times before passing from the field of the microscope.

As before mentioned, it is impracticable to calculate the intensity of the charge because the particles have no definite size or shape and they may form aggregates of varying complexity. The intensity of the charge is here measured by the speed of migration of only those particles which move. This introduces still another error in observations made on slow moving particles. Results are comparative and are presented only as such.

Figure 4 illustrates the effects of the various ions on the charge of the particles. It is evident that NaOH increases the charge to the greatest extent in the negative direction and that NaCl does not have quite so pronounced an effect. Ba, Ca and HCl decrease the charge and in dilute solutions, as does Al. But Al rapidly neutralizes the charge and even in dilute solutions reverses it to a marked extent. Only the most concentrated solutions of Ca and Ba reverse the charge of the particles, and HCl is more efficient in this regard than Ca or Ba. Increasing the concentrations of NaOH and NaCl decreases the charge of the particles. But this effect, as before pointed out, may be due to the internal friction of the solutions. When the concentration of Al is increased beyond 0.003 *M*, the charge is also decreased.

It was thought that some correlation between the intensity of the charge on the particles and the final volume of the sediment could be obtained from these experiments. That the degree of flocculation is independent of the sign or intensity of the charge is apparent from a comparison of the curves of figures 1 and 4. On the contrary, with Al, it seems that as the charge increases, the final volume of the sediment increases, but this statement does not hold for the other electrolytes. This condition is at variance with suspensions of the metals where the intensity of the charge determines the amount and speed of precipitation. There does seem to be some correlation between the intensity of the charge in either direction and the turbidity of the solution. Table 1 shows this quite clearly. It appears that flocculation with kaolin depends on the quantity and quality of the supernatant liquid. Calcium acts as a deflocculating agent on "chemically pure" kaolin as compared with the final volume of the kaolin in distilled water, although it decreases the charge on the particles. This statement is quite at variance with the generally accepted view.

DISCUSSION

Calcium is generally regarded as a flocculating agent in soils. The data presented indicate that it is a deflocculating agent on kaolin. There is no discrepancy in the two statements when it is considered that this paper deals with high resistance kaolin. Mattson (16) in discussing this question is of the opinion that calcium acts as a binder, or bridge between two particles of clay, holding them together. The number thus held increases with the pH, in this way hastening flocculation of the soil in question. It is believed that any effect that Ca may have as a flocculating agent is due only to the reduction in the effect produced by some electrolyte already present which has

deflocculated the soil to a greater extent than calcium is capable of doing. There is also the possibility of the precipitation of the hydrates of aluminum and iron, in this way binding together many clay and sand particles. Then too the flocculating effect of calcium on soils probably is not due directly to the effect on the soil particles but indirectly by the precipitation of silicates and humates.

The cataphoretic measurements reported by Dayhuff and Hoagland (5) in working with clay suspensions show the same general tendency as those given here. They say, in part,

> within the range of reaction found in the soil solutions, the clay colloid . . . . showed no change in the sign of its electric charge, and the nature and concentration of the cations present in the solution had a predominant influence on the stability of the colloidal suspension.

The observations of Dayhuff and Hoagland are in harmony with the present findings, with the single exception that 0.8 milliequivalents of aluminum as the chloride show a pronounced positive charge with kaolin. This is believed due to the greater purity of the kaolin used over the clay suspension of Dayhuff and Hoagland.

As before pointed out, HCl is adsorbed at all concentrations used and the nature of the curve indicates that HCl would be adsorbed even at infinite dilution. No other electrolyte used was adsorbed at dilute concentrations, but were "negatively adsorbed." The data presented indicate the "negative adsorption" sequence: NaCl, NaOH > Ba > Ca > Al.

The pH of the $AlCl_3$ solutions is very low. The hydrolysis of this salt would result in the liberation of a strong acid and a very weak base. It is then possible that it is the HCl which is adsorbed and not the molecule of the salt. The pH of the chlorides of calcium and barium is much higher, and adsorption does not begin until the solutions are comparatively concentrated. The hydrolysis of NaCl would result in the liberation of an equally strong base and acid, and as demonstrated by the curves, NaCl is least adsorbed by kaolin. It is unfortunate that pH determinations were not sufficiently accurate to indicate consistently the adsorption of the acid. Interpreted in this way, however, adsorption results are in accord with the work of Miller (19). In working with sugar charcoal, he comes to the conclusion that strong inorganic bases are "negatively adsorbed" and that adsorption from solutions of some salts is exclusively hydrolytic in nature, whereas from others, it is partially hydrolytic and partially molecular. Such conclusions are in accord with the theorem of Gibbs, that substances lowering the surface tension of a liquid are positively adsorbed at an interface, whereas those raising the surface tension tend to keep from the surface. This "negative adsorption" effect does not increase with the concentration. HCl decreases the surface tension of water whereas the other electrolytes used increase it. The work of Miller seems sufficient to explain the curves of figures 2 and 3.

In this regard, it is suggested that the theories of Harkins (7) together with the fixation effects of Langmuir's (11, 12, 13) secondary or residual valencies furnish some explanation of the phenomena of adsorption by kaolin. However, the data here presented are not sufficient to test their applicability.

From the above discussion, it would seem that adsorption is a function of pH and, as Loeb (14) has pointed out in his work on gelatine, when the pH is kept constant, there is no Hofmeister series. That his observations do not apply in the case of kaolin is apparent from figures 1 and 4. There can be no correlation between pH and flocculation when the curve for HCl is compared with any of the others, the flocculating tendency is the same, but the degree is vastly different. In the migration of the particles, neither the degrees nor the tendencies are similar.

There can be little question that each ion has its own specific effect on the particles with regard to degree of flocculation or deflocculation. That this affect is produced in the most dilute solution used is demonstrated by the curves of figure 1, despite the fact that the electrolytes used (HCl excepted) are "negatively adsorbed" at those concentrations.

The writer knows of no explanation that can adequately account for the phenomena described and only ventures the suggestion that Gibbs' Theorem is operative as described by Harkins and Miller, and that the effects of specific ions are due to their fixation to a greater or less extent at the surface because of the secondary of residual valencies described by Langmuir.

Figures 2 and 3 show conclusively that in the salt concentrations found in the soil, that is, concentrations of less than 0.003 M, the essential ions are not adsorbed by the particles of kaolin. At least, if any adsorption occurs at these concentrations, it is a negligible quantity. As Bouyoucos (2) has pointed out, this fact is opposed to the prevalent notion. He states in part,

> experimental evidence . . . . proved the opposite view, namely, the solution around the soil particles and in the very fine capillary spaces is less concentrated than the mass of the solution. All experimental evidence obtained is overwhelmingly in favor of this view.

SOLUBLE AND AVAILABLE ALUMINUM IN THE SOIL

From the data presented, it is clear that particles of clay are in a partially deflocculated condition at neutral pH and are progressively deflocculated as the pH increases. This statement is believed to apply only to soils with a high clay content. This is the only conclusion tenable in view of the successive solubilities of the mono-, di-, and tri-valent bases with decreasing pH. Another way of stating the condition, is that the soil is progressively flocked with increase in acidity. This flocculation, as before pointed out, is not due to the H-ion but rather to the ions brought into the soil solution as a result of the increasing acidity. It follows then that aluminum and iron are present in the soil solution in an easily soluble form in significant quantities at pH below 5.00.

In an effort to demonstrate that aluminum was present in significant quantities in solution at pH of from 4 to 5, the following experiment was performed. Stock solutions were prepared and determined and the following nutrient solutions were made by dilution:

$Ca(NO_3)_2$ ..... 0.016 and 0.008 *M*
$MgSO_4$ ..... 0.008 and 0.004 *M*
H_3PO_4 ..... 0.02 and 0.01 *M*
$Al_2(SO_4)_3$ ..... 0.002 and 0.001 *M*

To change the pH, a liter of the above nutrient was titrated with standard KOH. The curves are of exactly the same type as Clark (4) found in the titration of H_3PO_4 with normal KOH. The greatest value of the tangent is reached between pH 3.8 and 5.2. The exact amount of Al added per liter being known, analyses were made to determine the amount precipitated at various acidities. Insofar as no Fe was added, Al determinations could be made directly after separating off the Mg and Ca. To lose as little Al as

TABLE 2

Effect of dilution on Al solubility

pH of nutrient	Al in solution	
	2 × concentration	× concentration
	p.p.m.	*p.p.m.*
4.35	6.0	6.5
4.53	3.7	4.0
4.70	2.3	2.1
4.85	0.9	...
5.42	1.1	...

possible, the volumes were kept down to less than 75 cc. and precipitates were washed with as little water as possible, tests being made for Ca and Mg constantly. The pH of the precipitating reactions were kept below 7.0.

Analyses of the precipitate formed showed in both series practically the same amount of Al in solution. From table 2 it may be seen that dilution has no apparent affect on Al solubility.

The Al in solution could not possibly have any effect on the soil or kaolin particles with regard to their flocculation. Even if the method of analysis employed is assumed to give 100 per cent error, the quantities of Al in solution could cause no flocculation of the kaolin.

A search for the reason brought to light several articles that had been overlooked. A comparison of the determinations made by Magisted (15) for Al present in solution indicates that the quantity of soluble Al in solution is a function not only of pH but of PO_4 as well. Crone's nutrient, high in phosphoric acid, renders Al more insoluble, whereas the nutrient of Hartwell and Pember with only a small molar concentration of phosphoric acid equiva-

lent, increases the solubility of Al over that found in the nutrient reported in this paper.

Whether this view is the correct one can only be determined by further work. However, the experiments of Mirasol (20) indicate that this opinion is true. He found that the addition of acid phosphate reduced the toxicity of Al to plants and that the decrease in toxicity depended on the rate of acid phosphate application. Hartwell and Pember (8) observed that the amount of active Al is decreased by the increase of acid phosphate application despite the increase in the acidity of the soil so treated. From the determinations of Burgess (3) and Mirasol it seems that aluminum is present in the soil at low pH, not as the phosphate (unless phosphate was added) but as the nitrate, sulfate, or chloride. From their data it also seems that the quantities present depend on the nature and antecedents of the soil.

In order to obtain some estimation of the quantity of aluminum and iron present in the solution of the soil before reported upon (22) in connection with the formation of hardpan, the method employed by Blair and Prince (1)

TABLE 3

Analysis of 1 liter water extract from four soil samples

SOIL SAMPLE	pH	COMBINED ALUMINUM AND IRON
		p.p.m.
1	4.5	52
2	4.75	45
3	5.0	5
4	5.2	12

was used. Table 3 shows the results obtained by the analysis of 1 liter of the water extract obtained from 5 kgm. of four soil samples.

Two samples were taken from the southern part of the area in which hardpan was found, the pH being 4.5 and 4.75; and two samples were taken from the part of the area where hardpan was not found, the acidities being 5.0 pH and 5.2 pH.

The southern part of this area is greatly affected by quantities of smoke from neighboring factories and railroads.

This is believed to be the proof needed to support the theory of hardpan formation to be advanced. A comparison with the results of Blair and Prince show these values to be considerably higher than they obtained. Furthermore, soils 3 and 4 do not fall on a theoretical curve that can easily be imagined. It is probable that this is because of different quantities of phosphate present in those soils.

A THEORY FOR THE FORMATION OF HARDPAN IN ACID CLAY SOILS

The theories advanced relative to the formation of such hardpans have been based almost entirely upon the mechanical behavior of the soil parti-

cles—surface drying, precipitation of various cations because of supersaturation, the carrying down of small particles, and so on. These factors undoubtedly play a part, but in themselves are not sufficiently in accord with the facts observed in the case. Some years ago Warington (26) observed:

> Hydrated ferric oxide is another colloid substance which in sandy soils undoubtedly plays the part of a cementing agent. In rocks and soils of the Red Sandstone formations, its influence is plainly marked. Perhaps, however, the most obvious example of the cementing action of ferric oxide is afforded by the formation of iron-pan in Moor soils. . . . . The iron has been dissolved out of the surface soil by the action of humic acids . . . . passes in solution into the subsoil where is it precipitated, with the result that the sand at a certain depth is cemented together and an iron-stone produced.

Warington had little evidence in support of this view other than observation and did not mention that the same phenomena could obtain in clays as well. The evidence presented here supports his view and attempts to explain just how that layer comes into being.

It has been shown in the weak concentrations found in the soil solution that the essential salts necessary for plant growth are kept away from the surface of the clay fraction. This is in accord with the Second Law of Thermodynamics and the Theorem of Willard Gibbs. That the effects of the various cations in these concentrations, despite apparent non-adsorption, is evident has also been shown. The explanation suggested is that the residual valencies induce a weak chemical attraction such as Langmuir pointed out. HCl is greatly adsorbed by kaolin and according to Miller, this applies to other acids in the case of sugar charcoal. As shown in final volume of sediment curves, both HCl and Na_2SO_4 greatly deflocculate kaolin as compared to water. The tri-valent citrate ion is still more efficient in this regard. That mineral acids are present in the soil has been demonstrated by many workers.

Na and K are soluble at the lower acidities. As the pH decreases, calcium and magnesium are leached from the soil solution. This loss results in a further decrease in the pH which brings into the soil solution ion and aluminum. From the data presented, it is evident that at the lower pH, iron and aluminum do not generally exist as the phosphates in which condition they are insoluble. Rather they are present as chlorides, nitrates, or sulfates.

The hardpan observed and previously reported upon indicated that the first cause in its formation was the deposition of SO_2 blown by the prevailing winds across the area from factories and railroads. The closer to the railroads and factories, the more prevalent and well defined was the hardpan. It is reasonable to suppose that the decreased pH was due to the formation of sulfuric acid.

With regard to the clay fraction, deflocculation prevails at the higher pH because of the high molarity of the soil solution in salts that can dissociate clay aggregates. Undissociated particles are constantly being washed down by gravitational water and are deposited at various depths, depending on the mechanical condition of the soil. Attending this phenomena is the fall in

pH, and the pH increases with the depth of the soil. Kelly (10) has shown that the lowest pH is generally at a depth of five or six inches from the surface. Thus the surface soil will lose sodium and potassium, and latterly, magnesium and calcium to the soil at greater depths. The result is that the clay particles are carried farther and farther down because of deflocculation.

When the acidity at the surface is sufficient to bring into the soil solution aluminum and iron, the formation of a hardpan layer begins. This pH is something less than 5.0, but may be slightly higher depending possibly on the phosphates present.

The iron and aluminum in dilute solutions are not adsorbed by the clay and so in the soil solution are carried down and with the decrease in acidity are deposited farther from the surface. The progressively decreasing pH results in more and more iron and aluminum being brought into the solution until sufficient quantities are present to cause the flocculation of the collected dispersed clay particles at some depth, depending on the pH.

The aggregated clay particles cause the formation of a tight layer very slowly permeable to water. When this layer has dried out, aluminum and iron are deposited around the aggregates as the oxides, mechanically binding the entire mass together and effectively preventing the passage of water.

The analyses of the soil, where the hardpan was found, for combined aluminum and iron show that there is the equivalent of approximately .0015 *M* $AlCl_3$ present. Figure 1 shows that considerably less than this concentration brings about the maximum flocculation of kaolin and also that at about this concentration aluminum is adsorbed. At the part of the same area of ground where no hardpan was found, the equivalent of less than 0.00004 *M* $AlCl_3$ was analyzed.

These figures may also be interpreted as indicating the toxic properties of soluble aluminum.

SUMMARY

Kaolin being used as criteria for all clays, determinations have been made on the degree of turbidity of a supernatant solution, on the final volume of the sedimented kaolin when treated with various solutions, on the conductivity of solutions for adsorption data, and on the sign and intensity of the charge on the particles. These experiments are preliminary and the data are only presented for their comparative value.

Several concentrations of HCl, NaOH, NaCl, Na_2SO_4, $C_3H_5(COONa)_3$, $BaCl_2$, $CaCl_2$, $AlCl_3$, sucrose, and urea were used.

Different concentrations of the same electrolyte affect turbidities to a marked extent. Al clears the supernatant liquid in dilute solutions immediately after shaking, whereas the citrate and sulfate ions stabilize the suspension.

There is some correlation between turbidities and the final volumes of sediment. The most turbid solutions generally decrease the final volumes of

the kaolin to a marked extent, whereas nearly all the solutions of Al greatly increase the final volume.

Sucrose and urea have no affect on the kaolin whatever.

Of the ions used, Al and Na alone cause flocculation.

HCl is adsorbed at all dilutions to a great extent.

No other electrolyte used was adsorbed by the kaolin in the more dilute solutions.

A "negative adsorption" sequence is obtained: NaCl, NaOH > $BaCl_2$ > $CaCl_2$ > $AlCl_3$.

In concentrated solutions Al, HCl, and Ca and Ba reverse the sign of the charge on the particles most efficiently in the order given.

The degree of flocculation is apparently independent of the intensity of the charge on the particles.

Evidence is presented in support of the view that adsorption is not a function of pH in clays.

From the findings it seems that the amount of Al in a soluble form in the soil moisture depends on the amount of phosphate present in that soil as well as on the pH. That is, a great decrease in either may result only in a slight increase in the amount of Al present; a slight decrease in both will cause a great increase in the amount of Al and Fe in solution.

A theory is advanced to account for the formation of hardpan in acid clay soils.

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